Photodegradation of Methylene Blue Aqueous Solution Sensitized by Pyrochlore-Related κ -CeZrO₄ Oxide Powder

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The photocatalytic degradation of methylene blue aqueous solution sensitized by a pyrochlore-related κ -CeZrO₄ phase was investigated under irradiation with Xe discharge light. The optical absorbance of the solution was first decreased smoothly, and then retention was observed in several hours due to the formation of a new absorption peak. The absorbance spectrum resembled that of thionine. The present study confirms that the photocatalytic reaction sensitized by κ -CeZrO₄ was different from that by TiO₂.

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1. Introduction

Photo-oxidative degradation of organic substances needs strong oxidative power of photo-excited holes in a semiconductor, and therefore the energy of the valence band maximum of the semiconductor has been concerned as an important factor.¹⁻³⁾ Titanium oxide, TiO₂, has been used extensively, because of its relatively high photocatalytic activity and chemical stability.^{1,4,5)} However, another facet may exist in most of the oxidation of organic substances; that is, the supply of oxygen is needed to complete the oxidative degradation. From this view point, the authors have paid attention to κ -CeZrO₄ phase^{6,7)} as a potential photocatalyst, which can release oxygen smoothly even at temperatures as low as 573 K and therefore, has been used for oxidizing harmful automotive exhaust gases, *e.g.*, hydrocarbon and CO. The κ phase is an oxygen-inserted pyrochlore-related oxide,^{7,8)} which can be obtained by oxidizing pyrochlore-type Ce₂Zr₂O_{7+2 δ} at temperatures as low as 873 K. Because the oxidation proceeds retaining the respective ordered arrangement of Ce and Zr ions in it, the obtained κ phase is distinguished from fluorite-type (Ce_{0.5}Zr_{0.5})O₂ phase with random arrangement of the cations.^{8,9)} The κ phase is yellowish white, and absorbs light of longer wavelength than the titanium oxide, TiO₂ does. In this paper, the photocatalytic activity of κ phase was examined using the photodegradation of methylene blue aqueous solution.

2. Experimental Procedure

To obtain the κ -CeZrO₄ powder having a uniform distribution of Ce and Zr ions in it, the single phase of t'-(Ce_{0.5}Zr_{0.5})O₂ was first prepared by a conventional ceramic method. Powdered raw materials of CeO₂ (Na: <100 ppm, Fe: <10 ppm) and ZrO₂ (HfO₂: <3.8 mass%, Na: <100 ppm, Fe: <100 ppm), which were supplied by Santoku Kinzoku Kogyo Co., Ltd, were thoroughly mixed at a molar ratio of 1 : 1 using ball mill in zirconia container, and pressed into 17.2-mm diameter disks under 100 MPa. The disks were

sintered in air at 1923 K for 50 h to attain a single phase with a cubic CaF₂-type structure. When these were cooled by cutting the electric power off the furnace, the phase became single t'-(Ce_{0.5}Zr_{0.5})O₂.^{7,8)} After the t' pellets were crushed into grains, these were loaded in an alumina tube equipped in a conventional electric furnace. On passing Ar + 1%H₂ gas at a flow rate of 100 cm³min⁻¹, the sample was heated and kept at 1573 K for 10 h to obtain a pyrochlore-type Ce₂Zr₂O_{7+2 δ} precursor. After the precursor was cooled, pure O₂ gas was introduced. The sample was reoxidized at 873 K for 10 h in the O₂ gas to attain κ -CeZrO₄ phase. The obtained κ -CeZrO₄ phase was milled lightly for several minutes using a zirconia mortar, and then used as a photocatalyst sample powder.

A 2 × 10⁻⁵ mol·dm³ methylene blue aqueous solution (100 cm³) with the sample powders (0.20 g) was loaded in a glass container (with the inside area of 28 cm²) and stirred with a magnetic stirrer under irradiation with 500W Xe discharge light above the aqueous solution. After a preselected time had passed, 12 cm³ of the solution was aspirated and subjected to centrifugation. The optical absorption spectrum for the supernatant solution was recorded using a double-beam spectrophotometer (Hitachi U4000).

3. Experimental Results and Discussions

Figure 1 shows the X-ray diffraction pattern of the κ -CeZrO₄ powder prepared in this study. Fundamental diffractions for CaF₂-type structure and sharp diffractions with indices of all odd numbers of hkl and 422 were clearly observed; the diffraction pattern indicated the similar cations ordered arrangements to pyrochlore-type phase. Further, from many small superlattice diffractions, indicated by asterisk, the sample could be identified as a single phase of the κ -CeZrO₄.^{8,9)} Figure 2 shows the diffuse reflectance spectrum of the κ -CeZrO₄ powder, along with those of ZrO₂, CeO₂, and TiO₂ (ST-01, Ishihara Sangyo Co. Ltd.) powders. The κ -CeZrO₄ phase absorbed visible light of wavelength λ > 420 nm due to its fundamental absorption. Its absorption edge located at longer wavelength than those of ZrO₂ and CeO₂ being its constituent oxides; that is, the energy band gap of κ -CeZrO₄ is smaller than those of ZrO₂ and CeO₂. In

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Fig. 1 Powder XRD patterns for κ -CeZrO₄ phase prepared in this study.

Fig. 2 Diffuse reflectance spectrum of κ -CeZrO₄ phase compared with those of CeO₂, ZrO₂ and TiO₂.

view of the fact that the valence band maximum of ZrO₂ is more negative than that of TiO₂,¹⁰⁾ we have inferred that the valence band maximum of κ -CeZrO₄ phase may be lower than that of TiO₂.

Methylene blue aqueous solution absorbs light of around 664 nm, and shows bright blue. As is well-known, when the aqueous solution is subjected to the photocatalytic redox reactions sensitized by TiO₂, the characteristic absorption peak of methylene blue around 664 nm decreases smoothly^{11,12)} with a slight shift toward a shorter wavelength,¹³⁾ and the solution eventually becomes colorless. Figures 3(a) and (b) show variations in the absorbance spectra of the aqueous solution sensitized by the κ -CeZrO₄ powder, respectively, under unfiltered irradiation with Xe discharge light and irradiation with visible light of $\lambda > 420$ nm using UV-cut filter (L42, Suruga Seiki Co. Ltd.). In the both cases, for 4 or 5 hours after the irradiation was started, the characteristic

absorption peak of methylene blue around 664 nm decreased. However, after that, an absorption peak appeared around 580 nm and increased very slowly. As a result, the aqueous solution became light purplish blue. In Fig. 4, the maximum absorbance in the wavelength range of 600 to 664 nm for κ -CeZrO₄ powder is plotted against time, along with that for anatase-type TiO₂ powder (ST-01, Ishihara Sangyo Co. Ltd.). The photodegradation of methylene blue sensitized by TiO₂ proceeded very fast under unfiltered irradiation, and became negligible small under the irradiation with visible light of $\lambda > 420$ nm. In the case of κ -CeZrO₄ powder, difference in the rate of decrease between unfiltered irradiation and irradiation with visible light of $\lambda > 420$ nm appeared to be small. For the unfiltered irradiation, the absorbance spectrum at 4 h in the wavelength of 530 to 570 nm overlapped with that at 2 h. For the irradiation with visible light of $\lambda > 420$ nm, the absorbance values in the wavelength of 530 to 570 nm range decreased monotonously until 6 h. This result indicates that the rate of increase of absorption peak around 580 nm induced by the unfiltered irradiation was larger than that by irradiation with light of $\lambda > 420$ nm. A knick point on the decay curve for the κ -CeZrO₄ at around 3.5 h spent, appearing in Fig. 4, is attributable to the effect of the appearance of the absorption peak around 580 nm. Under irradiation with light of $\lambda > 500$ nm using UV-cut filter (Y50, Suruga Seiki Co. Ltd.), the photocatalytic activity of the κ -CeZrO₄ became negligible small. The dependence of the photocatalytic activity on the wavelength of the light irradiated is consistent with the diffuse reflectance spectrum of the κ -CeZrO₄ powder shown in Fig. 2. The change in the color of the aqueous solution is shown in Fig. 5.

The photo-bleaching of dyes, *e.g.*, methylene blue, proceeds by the irreversible degradation, *i.e.*, chemical reactions, and/or the reversible change to leuco-state. The former reactions are the example of decomposition of

Fig. 3 Variation in the absorption spectrum of methylene blue aqueous solution, sensitized by κ -CeZrO₄ powder, under irradiation with 500W Xe discharge light. The concentration of methylene blue in the starting solution was 2×10^{-5} mol·dm⁻³. (a): unfiltered irradiation, (b): irradiation with $\lambda > 420$ nm using L42 filter.

Fig. 4 Change in the maximum absorbance in the wavelength range of 600 to 664 nm of methylene blue under irradiation with 500W Xe discharge light. $\diamond$, $\blacklozenge$: TiO₂ powder dried at 413 K, $\circ$, $\bullet$: κ -CeZrO₄ powder, $\times$: without sample powder, $\diamond$, $\circ$: unfiltered irradiation, $\blacklozenge$, $\bullet$: irradiation with $\lambda > 420$ nm, $\bullet$: irradiation with $\lambda > 500$ nm.

polluted organic substances. The latter reversible change may be applicable for the usage as holographic memories. For this purpose, Pradeep and co-workers¹⁴⁾ have recently investigated change in absorbance spectrum of methylene blue sensitized gelatin film under He-Ne laser irradiation, and observed retention of the optical absorption change. The laser irradiation resulted in the formation of a new absorption peaks around wavelength of 600 nm, which matched with

thionine. The magnitude of the peak appearing under the irradiation for several ten minutes was still large as half of the maximum peak of the un-irradiated methylene blue. Such an irreversible degradation is harmful for application to optical memories; however, it may be applicable for a selective degradation of polluted organic substances.

In the present study, the peak formed by the irradiation was fairly smaller than that of methylene blue aqueous solution, and further its wavelength, *i.e.*, around 580 nm, differed slightly from that of thionine. The most of reactions sensitized by κ -CeZrO₄ may resemble that by TiO₂. Nevertheless, the present results imply that selective degradation of the methylene blue led to the retention in the optical absorption and the formation of another organic substance. The result may be attributed to the strong oxidizing power of κ -CeZrO₄ phase.

4. Conclusions

The photocatalytic degradation of methylene blue aqueous solution sensitized by a pyrochlore-related κ -CeZrO₄ phase was investigated under irradiation with Xe discharge light. The κ -CeZrO₄ phase was obtained by the oxidation of pyrochlore-type Ce₂Zr₂O_{7+2δ} precursor. The results obtained were as follows,

- (1) The κ -CeZrO₄ phase obtained was yellowish white and absorbed the light of $\lambda < 500$ nm. The absorption edge was located at longer wavelength than those of ZrO₂ and CeO₂.
- (2) Under unfiltered irradiation with Xe discharge light, the

Fig. 5 Variation in the colors of methylene blue aqueous solution sensitized by κ -CeZrO₄ powder under unfiltered irradiation with 500W Xe discharge light. (a) 0 h, (b) 4 h, (c) 8 h.

optical absorbance of methylene blue aqueous solution was first decreased smoothly. When using light-cut filters, for irradiation with light of $\lambda > 420$ nm, its decrease rate became slower. Under irradiation with light of $\lambda > 500$ nm, the photocatalytic degradation was negligible small.

- (3) In several hours, retention was observed due to the formation of a new absorption peak. The aqueous solution became light purple, and its absorbance spectrum resembled that of thionine.
- (4) The present study confirms that the photocatalytic reaction sensitized by κ -CeZrO₄ was somewhat different from that by TiO₂. The result may come from the strong oxidizing power of the κ phase.

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